SOP 13

Gravimetric calibration of volume contained using water

1. Scope and field of application

This procedure describes how to calibrate the volume of solution contained by a volumetric flask or other container capable of being filled to a reproducible mark. This is expressed as the volume contained at a standard temperature $(20.0\ ^{\circ}\text{C})$. This procedure is capable of achieving a reproducibility of better than 0.01% (1 relative standard deviation).

2. Principle

The mass of water contained by the flask at a measured calibration temperature is used to compute the volume of water contained at that temperature. The volume that would be contained at the standard temperature (20 °C) can be calculated by taking account of the volumetric expansion of the flask. The volume of liquid contained at any desired temperature can be calculated in a similar fashion.

3. Apparatus

- 3.1 Analytical balance capable of weighing the quantity of water contained with a sensitivity of 1 part in 10⁵ while having the capacity to weigh the water together with the container being calibrated.
- 3.2 Thermometer accurate to ± 0.1 °C

4. Reagents

4.1 Deionized water

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5. Procedure

- 5.1 Weigh the clean dry empty container together with the associated closure.
- 5.2 Fill the container being calibrated to the mark with deionized water, allowing the temperature of the container and contained water to reach an equilibrium value.

 Note this temperature.
- 5.3 Close the container and reweigh it.

6. Calculation and expression of results

6.1 Volume of the water contained at the calibration temperature Compute the weight of the water contained from the difference between weights of the filled and empty container:

$$w(H_2O) = w(\text{filled container}) - w(\text{empty container})$$
. (1)

Compute the mass of water contained, correcting for air buoyancy (see SOP 21):

$$m(H_2O) = w(H_2O) \left(\frac{1 - \rho(\text{air})/\rho(\text{weights})}{1 - \rho(\text{air})/\rho(\text{sample})} \right)$$
 (2)

The volume contained at the noted temperature, t, is

$$V(t) = m(H_2O) / \rho(H_2O, t)$$
 (3)

The density of air-saturated water in the temperature range 5 to 40 °C is given by the expression (Jones & Harris, 1992):

$$\rho_{\rm W} / (\rm kg \cdot m^{-3}) = 999.84847 + 6.337563 \times 10^{-2} (t/^{\circ}\rm C) - 8.523829 \times 10^{-3} (t/^{\circ}\rm C)^{2} + 6.943248 \times 10^{-5} (t/^{\circ}\rm C)^{3} - 3.821216 \times 10^{-7} (t/^{\circ}\rm C)^{4},$$
 (4)

where t is the temperature on ITS 90 (Note 1). To achieve an accuracy of 1 part in 10^4 , t must be known to within 0.5 °C.

$$t_{90} = 0.0002 + 0.99975 t_{68}$$
.

The small difference in temperature scales is typically not important to the calibration of glassware for the procedures in this Handbook.

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The International Practical Temperature Scale of 1968 (IPTS 68) has recently been superceded by the International Temperature Scale of 1990 (ITS 90). A simple equation can be used to relate the two over the oceanographic temperature range 0 to 40 °C (Jones & Harris, 1992):

6.2 Volume that would be contained at an alternate temperature To convert volume contained at one temperature (t_1) to a standard or alternate temperature (t_2) , we need to take account of the thermal expansion of the container being used. For pyrex-like glasses (Corning 7740, Kimble KG-33, Schott Duran, Wheaton 200, etc.) the coefficient of linear expansion α_l is 32.5×10^{-7} K⁻¹; for glasses such as Kimble KG-35, α_l is about 55×10^{-7} K⁻¹.

The coefficient of volumetric expansion,

$$\alpha_V = (1 + \alpha_l)^3 - 1 \approx 3 \alpha_l , \qquad (5)$$

is used to calculate the corrected volume at the alternate temperature:

$$V(t_2) = V(t_1) \left\{ 1 + \alpha_V (t_2 - t_1) \right\} . \tag{6}$$

This correction is negligible for all except the most precise work; unless $(t_2 - t_1)$ exceeds 10 °C or if plastic ware is used.

- 6.3 Example calculation
- 6.3.1 The following data were used for this calculation:

$$\begin{split} w({\rm H_2O}) &= 996.55~{\rm g}~,\\ {\rm calibration~temperature} &= 23.0~{\rm ^{\circ}C}~,\\ \rho({\rm H_2O},\,23.0~{\rm ^{\circ}C}) &= 0.997535~{\rm g\cdot cm^{-3}}~,\\ \alpha_l~{\rm is}~32.5\times 10^{-7}~{\rm K^{-1}}~,\\ {\rm weighing~conditions}\\ \rho({\rm air}) &= 0.0012~{\rm g\cdot cm^{-3}}~({\rm Note}~2),\\ \rho({\rm weights}) &= 8.0~{\rm g\cdot cm^{-3}}~. \end{split}$$

6.3.2 Correct weight of water to mass:

$$m(H_2O) = 996.55 \times \frac{1 - 0.0012/8.0}{1 - 0.0012/0.997535}$$

= 997.60 g.

6.3.3 Compute volume of water contained at the calibration temperature of 23.0 °C:

$$V(23.0 \, ^{\circ}\text{C}) = 997.60 / 0.997535$$

= 1000.07 cm³.

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This value is appropriate to measurements of moderate accuracy made at sea level pressure (1 atm) and at normal laboratory temperatures (\sim 20 °C). For a more accurate value see SOP 21, Equation (1).

6.3.4 Compute volume that would be contained at the standard temperature of 20.0 °C, *i.e.* the standard calibrated volume.

$$V(20.0 \,^{\circ}\text{C}) = 1000.07 \left\{ 1 + 3 \left(32.5 \times 10^{-7} \right) (20.0 - 23.0) \right\}$$

= 1000.04 cm³.

6.3.5 Compute volume that would be contained at 25 °C.

$$V(25.0 \,^{\circ}\text{C}) = 1000.04 \{1 + 3(32.5 \times 10^{-7})(25.0 - 20.0)\}$$

= 1000.09 cm³.

7. Quality assurance

To ensure that the volume contained is in control, the amount contained should be measured regularly and a property control chart maintained of the volume as corrected to 20 °C (see SOP 22).

References

Jones F. E. & G. L. Harris (1992) ITS-90 density of water formulation for volumetric standards calibration. *Journal of Research of the National Institute of Standards and Technology* **97**, 335–340.

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